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Information Sheet on THE SAMPLING AND ANALYSIS OF GASES IN CANS OF DEHYDRATED VEGETABLES

Western Regional Research Laboratory, Albany, California
Bureau of Agricultural and Industrial Chemistry
Agricultural Research Administration
U. S. Department of Agriculture

It is practically essential, in plants where dehydrated vegetables are gas-packed in cans in accordance with purchasing specifications, that provision be made for sampling and analyzing the gas in the packed cans. The purpose here is to describe the apparatus and procedures that have been found satisfactory for similar use in the Western Regional Research Laboratory. The carbon dioxide and oxygen contents of the gases are thereby determined with an accuracy of approximately 0.1 to 0.2 percent.

The Apparatus

The apparatus consists of (1) the gas sampling assembly and (2) a portable Orsat gas-analysis apparatus. With the exception noted later in a list of apparatus and supplies required, all this apparatus can be purchased from manufacturers of laboratory appliances.

1. The Gas Sampling Assembly is shown in Figure 1. Its base (A) is a steel plate 12 x 12 inches x $\frac{1}{2}$-inch thickness. Two metal rods (B) of half-inch diameter, length approximately 20 inches, are screwed into the base, approximately 10 inches apart. This clearance between the rods provides sufficient room for cans of sizes up to that of a standard 5-gallon can. A base of hard wood may be substituted, with lock nuts on the rods to fasten them firmly to the base. The metal rod (C), which carries the puncturing device, is held in position by the clamp holders (D) and can be raised or lowered to any desired height.

The can-puncturing device consists of a threaded tee (E), which supplies the force required to puncture the can, and the puncturing device proper (F). These are shown also in detail. The puncturing device is connected to a gas collection tube (G), of not less than 330 ml. capacity, by means of a glass capillary tube (bore 2 mm.) carrying a glass stopcock, joined to these by tightly fitting high-grade rubber tubing. The tube (G) is connected as shown to a leveling bulb (H) by heavy-wall rubber tubing, by means of which a liquid in G, preferably mercury, can be raised or lowered as desired. Mercury is required when the sampling of gas involves the creation of a high vacuum in G. If the degree of vacuum required for withdrawal of the gas sample into G is not high, as in the case of large cans, a solution of sodium sulfate (reagent A below) may be substituted for mercury.

The collection of the sample of gas from the can is carried out as follows: The can is placed in the stand, usually in an upright position. The puncturing device is placed in position upon the lid; the required connection is made to the sampling tube (G); and this tube and connections are filled with the mercury (or other fluid) up to the stopcock nearest the puncturing device by raising

the bulb (H). This stopcock (I) and the upper stopcock of tube G are then closed. The puncturing device is next forced down against the can sufficiently to effect a gas-tight contact of the rubber stopper with the metal surface, but not sufficiently to puncture the can. The leveling bulb (H) is then lowered enough to produce considerable vacuum in G, and the stopcocks previously closed are opened. Leaks due to imperfect contact of rubber stopper, or to other causes, will be indicated if the mercury drops much lower than the upper stopcock of G. If no leakage is thus shown, the puncturing device is forced down farther until puncturing of the can is shown by a rapid fall of mercury in tube G. The leveling bulb is now lowered still farther as required for the collection of sufficient sample for analysis. Ordinarily a volume of approximately 150 ml. will be available from a No. 2 can containing gas at atmospheric pressure by lowering H approximately 15 inches. The stopcocks are then closed, and bulb H is raised until the gas sample is under a pressure of approximately $\frac{1}{2}$-inch of mercury. The sampling tube is then disconnected from the capillary connection and connected to the Orsat gas-analysis apparatus.

When the can from which a sample of gas is to be removed is a small one, such as a No. 2 can, it should be placed within a slightly larger open can, and when the rubber stopper of the puncturing device has been brought to apparently gas-tight contact with the can in the manner described above, the open can should be filled with water to a height sufficient to cover the stopper. In this way leakage of air by way of the stopper can be detected when the assembly is subjected to reduced pressure. Such leakage is not probable if the test described is found to be negative. Where large cans are sampled this precaution is unnecessary, because samples of gas can be collected without the production of any considerable vacuum.

2. The Orsat Gas-Analysis Apparatus (Figure 2). This consists of the following parts: A gas burette (A) enclosed in a water-jacket (B), which prevents serious error in measurement of gas volumes due to changes in temperature during an analysis; three absorption pipettes of the two-compartment type, the first (C, nearest the burette) for the absorption of carbon dioxide, the second (D) for the removal of oxygen, and the third (at left in Fig. 2) for such requirements as may develop (only two pipettes being required when only carbon dioxide and oxygen are to be absorbed); the glass manifold connecting the burette to the pipettes and with the outside of the apparatus through a three-way stopcock at the end of the manifold farthest from the burette.

The burette has a total capacity of 100 ml., 50 ml. of which is contained in the enlargement between the zero and the 50 ml. marks. The remaining 50 ml. of volume is contained in the length of the burette below the enlargement, and this is graduated in 0.2 ml. volumes. The confining liquid in the burette is the same as that referred to as a possible substitute for mercury in the collection of sample (reagent A).

The pipette for absorption of carbon dioxide contains a solution of potassium hydroxide (reagent C), and that for oxygen a pyrogallol solution (reagent D).

The analysis of the gas sample is conducted in the following manner: The gas sample tube (G) containing the sample is connected to the projecting end of the manifold through a capillary tube bent at right angles. The ends of the

capillary tube must be brought to close contact with the sample tube and the manifold. The manifold and all uncalibrated portions of the Orsat apparatus must first be filled with nitrogen. This is readily accomplished by introducing into the apparatus a sample of air, and removing in succession its carbon dioxide and oxygen as in an actual analysis. If this operation is carried out accurately, it will provide also a means of checking on possible leakage of apparatus, because, in the absence of leakage, the oxygen content as thus determined should be close to 20.9 percent. It is not necessary to repeat this operation in successive analyses when a sufficient residue of nitrogen remains in the burette after a previous analysis.

When a gas low in carbon dioxide is to be analyzed, the residual nitrogen in the burette is ejected through the three-way stopcock by raising the leveling bottle (E) and bringing the confining liquid to the zero mark. Before transfer of sample into the burette for analysis, a small quantity must be ejected into the air through the three-way stopcock of the Orsat manifold in order to sweep out air or other gas in the connections. The sample is then brought in by raising the leveling bulb (H) of the sample tube (G) and lowering the bottle (E) until approximately 100 ml. of sample has been introduced. The volume of sample is read carefully after the surface of the liquid in bottle E has been brought to the same level as that in the burette.

The sample in the burette is then passed into the hydroxide solution in the first pipette by raising the leveling bottle, and returned to the burette by lowering the bottle. This operation is repeated until the reading of volume becomes constant. With the reagent described for the purpose, three passes are ordinarily sufficient when the solution is fresh, but more passes will be required as the absorptive capacity of the solution is decreased by use.

After removal of all carbon dioxide, the gas is passed in the same manner into the pyrogallol solution to remove oxygen. Approximately the same number of passes of gas is required here as for the carbon dioxide determination. To compute percentage volumes of carbon dioxide and oxygen, the volume absorbed in each of these determinations is divided by the total gas volume analyzed. Nitrogen is estimated by difference.

When the gas to be analyzed is high in carbon dioxide it is necessary to dilute it with nitrogen free from this constituent and oxygen. For this purpose not less than 50 ml. of the residual nitrogen is retained in the burette, and the sample to be analyzed is then drawn in as previously described until the total volume in the burette is approximately 100 ml. The difference between total volume and the volume of residual nitrogen previously measured is the volume of gas sample analyzed. Percentages of carbon dioxide, oxygen, and nitrogen are computed as before.

Reagents Required

Reagent A. A solution of 100 grams of anhydrous sodium sulfate, 20 ml. of concentrated sulfuric acid, in 400 ml. of distilled water, with the addition of a few drops of methyl orange indicator.

Reagent B. A stock solution of potassium hydroxide, made by dissolving 800 grams of C. P. potassium hydroxide in distilled water to a volume of 1000 ml.

Reagent C. Potassium hydroxide solution used in analysis for carbon dioxide. Approximately 160 to 180 ml. will be required for one filling of pipette.

Dilute 100 ml. of the stock solution with 60 ml. of water. In these proportions, prepare the volume of solution required for filling the front compartment of the pipette completely and the rear compartment to a height of about one inch. Cover the liquid surface in the rear compartment with about $\frac{1}{2}$-inch thickness of refined mineral oil. This layer of oil protects the solution better than the rubber balloons commonly supplied with an Orsat apparatus.

Reagent D. Pyrogallol solution for absorption of oxygen. To make up this solution, first ascertain the volume of solution required for the pipette, i.e., for filling the front compartment completely and the rear compartment to a height of about one inch. Now transfer to the rear compartment the estimated volume of stock solution (reagent B). Cover the exposed liquid in the pipette with $\frac{1}{2}$-inch of the mineral oil. The weight of pyrogallic acid required is 15 grams to 100 ml. of stock solution (B). Dissolve the calculated weight in hot water, using 10 ml. of water for each 15 grams of pyrogallic acid. Insert below the oil layer the stem of a warmed glass funnel, and then pour in the pyrogallic solution slowly. The oil prevents rapid oxidation of the alkaline pyrogallol solution by contact with air, and takes the place of a rubber balloon. The mixing of the pyrogallol with the strong hydroxide in the pipette may be accelerated by drawing the liquids back and forth several times from one compartment to the other.

Itemized List of Apparatus and Supplies Required (with necessary purchase specifications)

1. Can-puncturing device. This item is not at present available on the market, but can be constructed easily by a competent mechanic. It will be necessary also to construct the support for this device. With this exception, all the items of this list can be purchased from manufacturers of laboratory apparatus and supplies.

2. Orsat apparatus. Complete. Supplied with burette, water jacket, leveling bottle, three plain absorption pipettes of the two-compartment type, the first compartment of which is filled with glass tubes, a manifold of heavy capillary tubing held in place by special, two-piece, nickel-plated metal holders with rubber cushions to protect the glass, and approximately 3 feet of rubber tubing connecting burette to leveling bottle. The portable case should be made of hard wood, with front and rear sliding panels.

The manifold should be provided with three two-way stopcocks of small bore, and a three-way stopcock at the inlet. The burette should have a total capacity of 100 ml., including a 50 ml. enlargement and a 50 ml. graduated length, the graduations to be in 0.2 ml. volumes.

3. Metal ware. One support stand for apparatus; rectangular base, 6 x 9 inches; rod, diameter 7/16-inch, length 24 inches. Two ring clamps for supporting gas-collection tube, nickel plated cast brass or iron, with slot in front, circular prongs covered with rubber, O. D. 2 inches.

One ring clamp, as above, O.D. 3 inches.

Two regular-model clamp holders, capable of gripping rods up to 1/16-inch.

4. Glassware. One leveling bulb, pyrex glass, with tubulation for rubber tubing connection, capacity approximately 500 ml.

One glass stopcock, pyrex, three-way, T-shape; solid stopper, bore of stopper 2 mm.; bore of capillary side arms, 2 mm., O. D. approximately 7 mm.

One gas collecting tube, pyrex, with two-way stopcocks, preferably with oblique bore, capacity 330 to 350 ml. (Such a tube of this capacity may have to be made to order. The alternative is to purchase, at somewhat greater cost from stock, a tube of description following.)

(Alternate). One gas-collecting tube, with three-way stopcocks, capacity 330 ml., pyrex. Bore of stopcocks and capillary tubing, 3 mm.; length of tube, 310 mm.; internal diameter, 63 mm.

5. Rubber goods. Three feet of rubber tubing, pressure and vacuum, red, of high quality and flexibility; internal diameter 3/16-inch; thickness of walls 3/16-inch.

One rubber stopper, one-hole, best quality, standard, size No. 3 or No. 4.

6. Chemicals:

Mercury, redistilled, 10 lbs.

Anhydrous sodium sulfate, C.P., 1 lb.

Sulfuric acid, concentrated, small quantity.

Methyl orange indicator.

Potassium hydroxide, C.P., pellets preferred, 5 lbs.

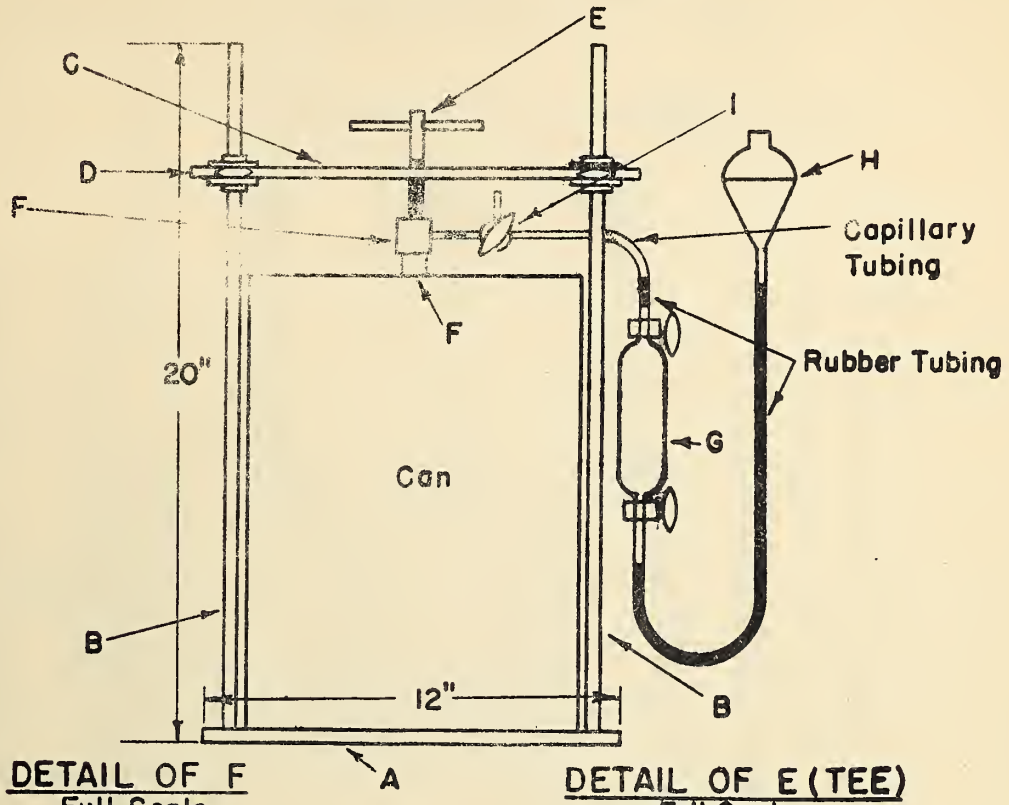
Pyrogallic acid, U.S.P., $\frac{1}{4}$ to $\frac{1}{2}$ lb.

Mineral oil, small quantity.

FIGURE 1

GAS SAMPLING ASSEMBLY

Scale 1" = 5"



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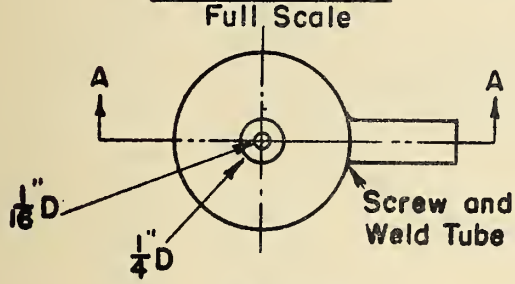
Full Scale



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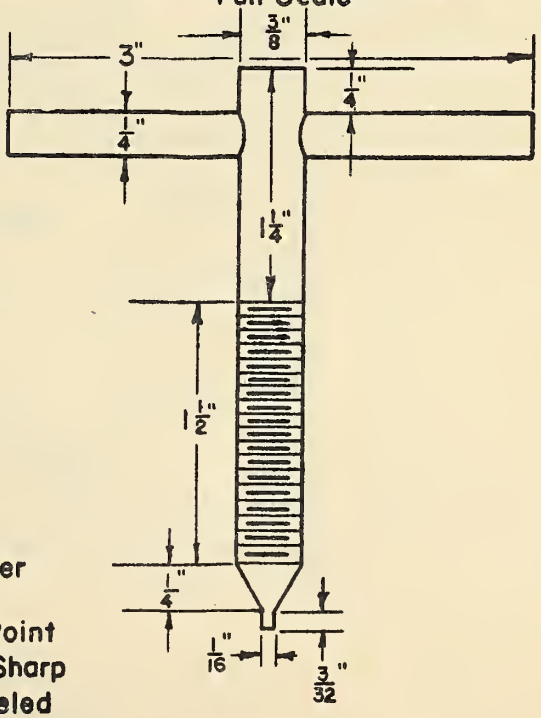
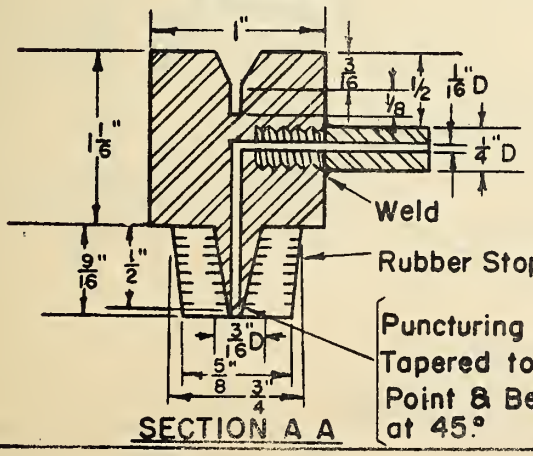


TOP VIEW



SECTION A A

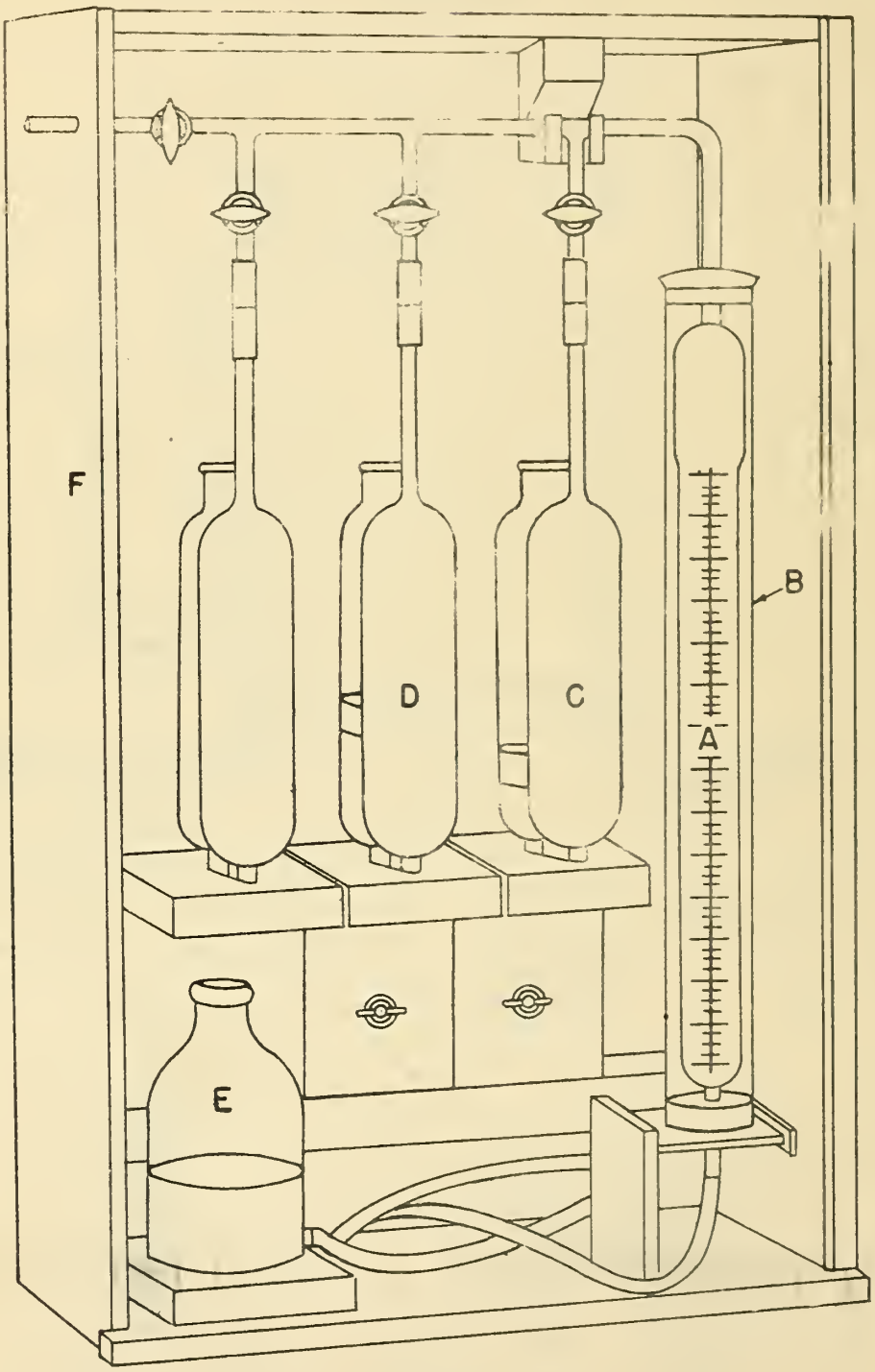


FIGURE 2
ORSAT APPARATUS